

## THE AMORPHOUS PHASE IN PLASMA SPRAYED HYDROXYAPATITE COATINGS

K.A. Gross and C.C. Berndt

The Thermal Spray Laboratory, Department of Materials Science and Engineering  
State University of New York at Stony Brook, NY 11794-2275, USA.

### ABSTRACT

Atmospheric plasma spraying of hydroxyapatite was carried out to investigate the influence of the plasma spraying parameters on the formation of the amorphous phase. The amorphous phase was investigated with X-ray diffraction and optical microscopy. The results infer that dehydroxylation of the molten particle and a high cooling rate produce a larger amount of the amorphous phase. Crystalline regions of the coating consist of partially molten particles and elongated recrystallized areas. The amorphous phase is commonly found at the substrate interface. It is shown that the amorphous regions vary throughout the coating which clinically could affect the process of bone deposition and successful implant fixation.

### INTRODUCTION

Atmospheric plasma spraying is used for applying hydroxyapatite to dental implants and orthopedic prostheses. The feedstock in the form of a powder is fed to the plasma and accelerated to about 150 m/s before impacting the substrate [1]. These high impact velocities flatten the molten particles and cause rapid heat flow to the substrate. This results in a very fast cooling rate ( $> 10^5 \text{°K/sec}$ ) which is **sufficient** to form an amorphous phase.

Crystallinity has been interpreted in different ways in the biomedical community. It was initially used as an indication of the crystal size or perfection of the crystal lattice in hydroxyapatite crystals [2]. Thermally sprayed material typically have a small grain size and a high defect concentration due to the fast cooling rate, in addition to a residual stress. These variables give rise to a broadening of the X-ray diffraction peak, making it comparable to the spectra of the inorganic phase in bone, Fig. 1. A high crystallinity hydroxyapatite material is included as a reference.

The performance of a thermally sprayed hydroxyapatite coating depends upon the chemical phases and their distribution within the microstructure. A **fine** grain size has been shown to give a higher dissolution [3] and the residual stress further modifies the properties. The influence of these factors with respect to the clinical functionality of the

implant has yet to be determined. The amorphous phase has been shown to dissolve more quickly than the crystalline phase [4,5], and could lead to coating degradation [6].

The purpose of this paper is to focus on the amorphous phase represented by the broad diffuse peak in the x-ray diffraction pattern of Fig. 1. The formation of such amorphous phases and their location within the coating is important knowledge with regard to designing a coating with the desired properties, such as a functionally graded coating.

## MATERIALS AND METHODS

A Metco 3MB plasma spray torch, with a GH nozzle was used to prepare hydroxyapatite coatings. Powder with a **Ca/P** ratio of 1.67, and a particle size distribution of 5 to 40  $\mu\text{m}$  was sprayed under different conditions. Initially, the powder was sprayed at different power levels to ascertain the changes taking place in the material upon entering the plasma. When this was determined, various plasma spraying parameters were altered to investigate the effect on amorphicity. The parameters that were changed include stand-off distance (5 to 20 cm), particle size distribution (the small particle sized powder was mixed with a larger particle size powder with a mean of 80  $\mu\text{m}$ ), substrate angle (0 to 60 degrees), gas flow rate (35 to 55 slpm), air cooling of the coating and hydroxylation state of the starting powder. A powder with a lower hydroxyl content was produced by heating at 1200°C for one hour followed by sieving. A substrate angle of 90° represents a substrate with the face positioned perpendicular to the stream of molten droplets.

The calcium and phosphorus concentrations were determined with X-ray fluorescence using a hydroxyapatite powder as a reference. Coating crystallinity was ascertained with a calibration curve produced by measuring the crystalline peaks and the broad amorphous peak of standard mixtures.

Coatings were sectioned on a diamond cut-off wheel, mounted in epoxy resin, ground and polished using 0.05  $\mu\text{m}$  alumina as the last step. The crystalline regions were viewed in the optical microscope using the **Nomarski** interference method to increase the depth of field and contrast of the features.

Two coatings with 98 wt.% amorphous phase were heated to 660 °C for 5 minutes in either dry or moist helium gas. The crystallinity was then measured using x-ray diffraction to ascertain the influence of the water content on the crystallization.

## RESULTS AND DISCUSSION

The coatings produced at various power levels showed that decomposition takes place at higher temperatures. At lower power levels tricalcium phosphate (TCP) will appear but more severe heating will also produce tetracalcium phosphate (TTCP) and calcium oxide. The former two phases are the equilibrium phases at high temperature and low partial water pressure. The **Ca/P** molar ratio also increases, **signifying** preferential removal of the phosphate group from the hydroxyapatite structure in more intense heating conditions, Table 1. This calcium rich molten particle solidifies to form calcium oxide along with the two calcium phosphate phases predicted by the **equilibrium** phase diagram.

As the spray angle deviates from perpendicular to the spray stream by more than 30°, an increase in the amorphous nature of the coating is noted, Fig. 2. Less **unmolten** particles participate in the buildup of the coating as they ricochet **from** the surface, but more importantly, the lamellae thickness decreases, as evidenced from studies on other materials [7]. This leads to a higher cooling rate and is associated with an increase in amorphousness of the coating. Heat flow through the substrate material will be higher than

Table 1. Influence of power level on the decomposition of hydroxyapatite.

Power Level (kW)	18	25	30	35
Ca/P molar ratio	1.67	1.69	1.75	2.03
Phases	HAp, TCP	HAp, TCP	HAp, TTCP, CaO	

to the surrounding air, however convectional cooling of the coating offers a secondary means to increase the cooling rate.

The composition of the hydroxyapatite also influences the formation of the amorphous phase. Use of a slightly dehydroxylated powder increases the amorphicity of the coating. A hydroxyl deficient molten particle will more likely form an amorphous phase compared to a droplet with a high hydroxylation level. The hydroxyl ion concentration of the molten particle before impact can be controlled by increasing the amount of heat transferred to the particles. For example, using a smaller particle size or a larger spraying distance facilitates this compositional change with a larger heat transfer to the particles. Also, a lower gas flow rate gives rise to slower particle velocities and a higher heat transfer. However, only part of the dehydroxylated droplet forms the **amorphous** phase, the remaining portion forming oxyapatite. This effect is most easily observed as the left shoulder on the **004** reflection in the X-ray diffraction pattern, inset of Fig. 3.

The penetration of X-rays is dependent upon the energy of the beam. X-rays will not penetrate through the entire thickness of the coating. Observation of the microstructure is important in determining the properties of the material and can be used to **identify** the size, shape and location of the crystalline regions within the coating. Figure 4 shows the microstructure of a **50 wt.%** and **100 wt.%** crystalline coating, as determined by X-ray diffraction. A noteworthy feature is the amorphous phase (darker grey in color) which very often forms at the titanium substrate. This is important in the performance of the coating. Other phases such as tricalcium phosphate are present in small quantities, however this cannot be distinguished **from** the hydroxyapatite.

The crystalline phase consists of **unmolten** or partially molten **particles** and recrystallized particles. The former is represented by the angular particles. The elongated crystalline particles (arrow on Fig. 4 and Fig. 6) are recrystallized regions, which can be explained by another short experiment. The heat **treatment** of the amorphous phase shows complete crystallization in a wet atmosphere but partial crystallization in a dry atmosphere, Fig. 5. Thus the molten droplet will consist of a hydroxyl rich core surrounded by hydroxyl deficient regions as it spreads out to form the lamellae. These two regions are inseparable and are both identified as the amorphous phase. The heat in the coating is dissipated slowly due to the low thermal diffusivity ( $\sim 5 \times 10^{-8} \text{ cm}^2/\text{s}$ ) and is elevated by additional heat given off in the structural relaxation of the amorphous phase. When the temperature is sufficiently high, recrystallization will first take place in the hydroxyl rich areas; hence the presence of elongated crystalline regions.

As consecutive layers are deposited, the heat in the coating may build up slowly and lead to crystallization in different places within the coating. The coating is more crystalline at the surface compared to the area adjacent to the substrate, Fig. 6, and

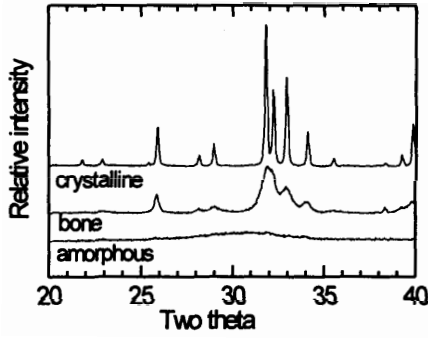


Figure 1. An X-ray **diffraction** pattern illustrates a) high crystallinity hydroxyapatite, b) inorganic bone and c) an amorphous phase found in hydroxyapatite coatings.

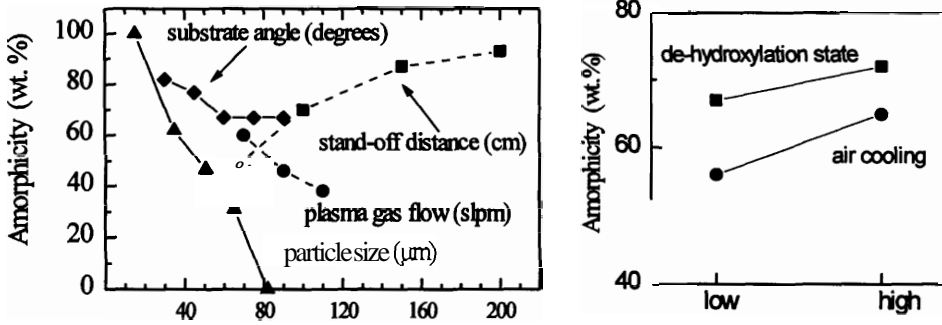


Figure 2. Influence of spray parameters on the amorphicity of the coating. (Abscissa is variable according to values or level of parameter).

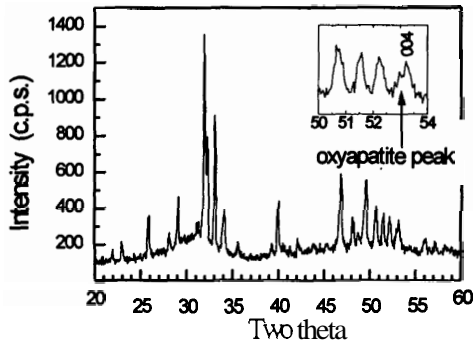


Figure 3. X-ray **diffraction** pattern showing the presence of the crystalline hydroxyapatite, oxyapatite and the amorphous phase.

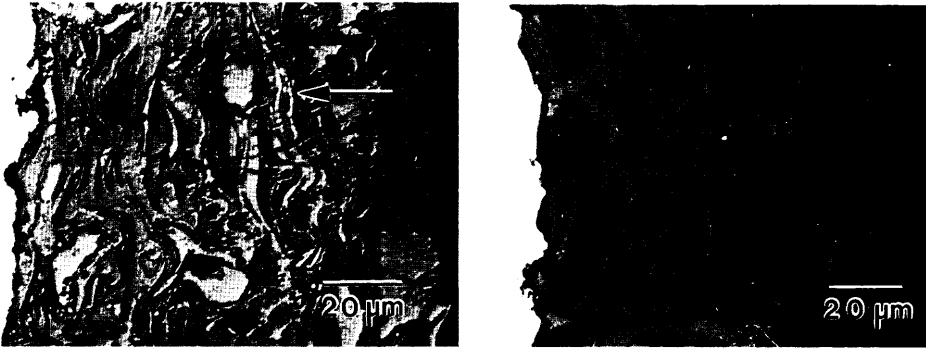


Figure 4. Microstructure showing the crystalline phase (indicated by higher plateaus of lighter color) in a 50 wt.% and 100 wt.% crystalline coating calculated from X-ray diffraction. (The titanium substrate is situated on the left hand side).

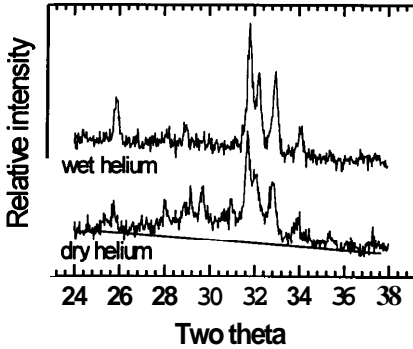


Figure 5. X-ray diffraction of the amorphous phase after heat treatment at 660 °C for 5 minutes in a dry and moist atmosphere.

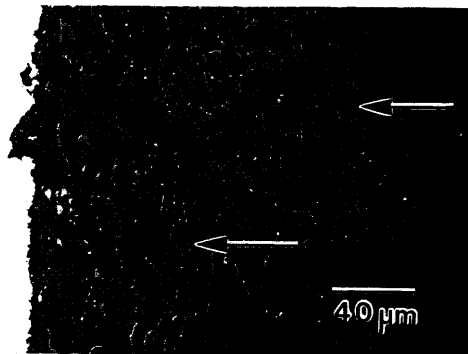
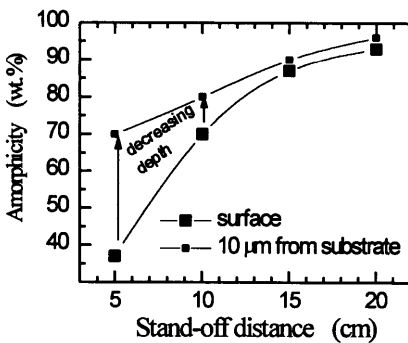


Figure 6. The variation of crystallinity close to the substrate and on the surface of the coating as identified by X-ray diffraction and shown in a micrograph.

becomes less noticeable with longer stand-off distances. The number of crystalline regions identified as recrystallized hydroxyapatite increases with thickness.

## CONCLUSIONS

Plasma spray processing of hydroxyapatite is very sensitive to the spraying parameters. It has been shown that the crystalline phase consists of **unmolten** and recrystallized areas within the coating. The amorphous phase forms as a result of dehydroxylation taking place in the particle during spraying and the fast cooling rate at the substrate. Optical microscopy is suitable for discerning crystalline regions within the coating. The distribution of the crystalline phase is modified by a rise in temperature and form crystallinity-graded regions within the coating.

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## REFERENCES

1. Knight, R., Smith, R.W. and Xiao, Z., Proc. 7th Nat. **Therm.** Spray Conf., 1994, 331-337.
2. Le Geros, R., *Clinical Materials*, 1993, 14, 65-88.
3. Lelievre, F. and Bernache-Assolant, D., Proc. 4th World Biomaterials Congr., Berlin, 1992, 330.
4. Gross, K.A. and Berndt, C.C., *J. Mat. Sci.: Mat. in Med.* 1994, 5, 219-224.
5. Klein, C.P.A.T., Wolke, J.G.C., Blicek-Hogervorst, J.M.A., de Groot, K., *J. Biomed. Mater. Res.*, 1994, 28, 961-967.
6. Bauer, T.W., Geesink, R.G.T., Zimmerman, R. and McMahon, J.T., *J. Bone Joint Sur.*, 1990, 3A, 1439-1452.
7. Montavon, G., Sampath, S., Berndt, C.C., Herman, H. and Coddet, C., *J. Thermal Spray Technol.*, 1995, 4, 67-74.